

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C07C 17/087, 17/21, 17/23	A1	(11) International Publication Number: WO 99/51553
		(43) International Publication Date: 14 October 1999 (14.10.99)
<p>(21) International Application Number: PCT/US99/07230</p> <p>(24) International Filing Date: 1 April 1999 (01.04.99)</p> <p>(30) Priority Data: 60/080,708 3 April 1998 (03.04.98) US</p> <p>(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(72) Inventors; and (73) Inventors/Applicants (for US only): MANOUE, William, H. [US/US]; 224 Revery Road, Newark, DE 19711 (US). NAPPA, Mario Joseph [US/US]; 3 Oakridge Court, Newark, DE 19711 (US). SMIVERT, Allan, Capron [US/US]; 215 River Lane, Elkton, MD 21921 (US)</p> <p>(74) Agent: HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, DE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, AR, PO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Russian patent (AM, A7, BY, KG, BZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BI, CF, CG, CI, CM, GA, GN, GW, ML, MR, NG, SN, TD, TO).</p> <p>Published With international search report.</p>
(54) Title: PROCESS FOR THE PRODUCTION OF FLUOROCARBONS		
<p>(57) Abstract</p> <p>A process is disclosed for the manufacture of hexafluoropropylene and 1,1,1,2,3,3,3-heptafluoropropane. The process involves (a) feeding 1,1,2-trichloro-3,3,3-trifluoropropene-1, HF and Cl₂ to a first reaction zone containing a catalyst comprising trivalent chromium and operating at a temperature of at least 250 °C, but not more than about 325 °C, to produce a reactor effluent comprising C₃H₂F₆, C₃HClF₅, CF₃CClF₂, HCl and HF. The reactor effluent of (a) may be distilled to produce (i) a low boiling stream including HCl; (ii) C₃H₂F₆, CF₃CClF₂, HCl and HF. The reactor effluent of (a) may be distilled to produce (i) a low boiling stream including HCl; (ii) a reactant stream including an azeotrope of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane and HF and (iii) a high-boiling stream including C₃H₂F₆ and C₃HClF₅. The 2-chloro-1,1,1,2,3,3,3-heptafluoropropane of reactant stream (ii) may be reacted with hydrogen in the presence of a catalyst to produce a mixture of hexafluoropropylene and 1,1,1,2,3,3,3-heptafluoropropane. While the C₃H₂F₆ and C₃HClF₅ of high boiling stream (iii) may be fed along with HF to a second reaction zone containing a catalyst comprising trivalent chromium and operating at a temperature of at least about 375 °C to produce a reaction product comprising C₃H₂F₆ and HF. The reactor product from the second reaction zone may be recycled to the first reaction zone.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LE	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SE	Sweden
AE	Archeria	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TC	Togo
BB	Barbados	GF	Guam	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MO	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ME	Republic of Macedonia	TR	Turkey
BG	Bulgaria	HR	Croatia	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	HU	Hungary	MN	Mongolia	UA	Ukraine
BR	Brazil	IE	Ireland	MR	Mauritania	UG	Uganda
CA	Canada	IL	Israel	MW	Malawi	US	United States of America
CF	Central African Republic	IT	Italy	MX	Mexico	UZ	Uzbekistan
CG	Congo	JP	Japan	NE	Niger	VN	Viet Nam
CH	Switzerland	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CJ	Cote d'Ivoire	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CM	Cameroun	KR	Democratic People's	NZ	New Zealand		
CN	China	KT	Republic of Korea	PL	Poland		
CU	Cuba	KZ	Republic of Korea	PT	Portugal		
CZ	Czech Republic	LC	Czechia	RO	Romania		
DE	Germany	LI	Liechtenstein	RU	Russian Federation		
DK	Denmark	LS	Lesotho	SD	Sudan		
EE	Estonia	LR	Liberia	SE	Sweden		
				SG	Singapore		

WO 99/51553

PCT/US99/07230

TITLE
PROCESS FOR THE PRODUCTION
OF FLUOROCARBONS
FIELD OF THE INVENTION

5 The present invention relates to the synthesis of hexafluoropropylene and 1,1,1,2,3,3,3-heptafluoropropane.

BACKGROUND

Commercial methods for the preparation of hexafluoropropylene ($\text{CF}_3\text{CF}=\text{CF}_2$ or HFP), a fluoromonomer, typically involve temperatures greater than 600°C . The high reaction temperatures lead to the formation of perfluoroisobutylene, an extremely toxic compound which is costly to remove and destroy (e.g., see European Patent Application No. 002,098). Processes for the manufacture of HFP at lower temperatures based on the use of acyclic three-carbon hydrocarbons or partially halogenated three-carbon hydrocarbons are disclosed in U.S. Patent Nos. 5,043,491, 5,057,634 and 5,068,472.

15 1,1,1,2,3,3,3-Heptafluoropropane ($\text{CF}_3\text{CHF}_2\text{CF}_3$ or HFC-227ea), a fire extinguishant, can be prepared by the reaction of HF with HFP in contact with activated carbon (e.g., see British Patent Specification No. GB 902,590). The manufacture of HFC-227ea in this instance is tied to the availability HFP.

20 There is a need for alternative methods of manufacturing HFP and HFC 227ea.

SUMMARY OF THE INVENTION

A process is provided for the manufacture of hexafluoropropylene and 1,1,1,2,3,3,3-heptafluoropropane. The process comprises (a) feeding 1,1,2-trichloro-3,3,3-trifluoropropene-1 ($\text{CCl}_2=\text{CClCF}_3$), HF and Cl_2 to a first reaction zone containing a catalyst comprising trivalent chromium and operating at a temperature of at least 250°C , but not more than about 325°C , to produce a reactor effluent comprising $\text{C}_3\text{Cl}_2\text{F}_5$, $\text{C}_3\text{Cl}_2\text{F}_6$, $\text{CF}_3\text{CClF}_2\text{CF}_3$, HCl and HF; (b) distilling the reactor effluent of (a) to produce (i) a low boiling stream comprising HCl, (ii) a reactant stream comprising an azeotrope of 2-chloro-1,1,1,2,3,3,3-heptafluoropropane HF and (iii) a high-boiling stream comprising $\text{C}_3\text{Cl}_2\text{F}_6$ and $\text{C}_3\text{Cl}_3\text{F}_5$; (c) reacting the 2-chloro-1,1,1,2,3,3,3-heptafluoropropane of reactant stream (ii) with hydrogen in the presence of a catalyst to produce a mixture comprising hexafluoropropylene and 1,1,1,2,3,3,3-heptafluoropropane; (d) feeding the $\text{C}_3\text{Cl}_2\text{F}_6$ and $\text{C}_3\text{Cl}_3\text{F}_5$ of high boiling stream (iii) along with HF to a second reaction zone containing a catalyst comprising trivalent chromium and operating at a temperature of at least about 375°C to produce a reaction product comprising $\text{CF}_3\text{CClF}_2\text{CF}_3$ and HF; and (e) recycling the reaction product of (d) to the first reaction zone.

WO 99/51553

PCT/US99/07230

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic flow diagram of an embodiment of the process of this invention.

DETAILED DESCRIPTION

5 The present invention involves the use of $\text{CCl}_2=\text{CClCF}_3$ and $\text{CF}_3\text{CClFCF}_3$ in combination as materials for producing $\text{CF}_2=\text{CFCF}_3$ and $\text{CF}_3\text{CHFCH}_2\text{F}$. The process of the invention uses an azeotropic composition of $\text{CF}_3\text{CClFCF}_3$ and HF as a precursor to the desired products. Further information on such azeotropes is provided in U.S. Patent Application No. [CL-1158-P1], which is hereby
10 incorporated by reference herein.

$\text{CCl}_2=\text{CCl}_2\text{CF}_3$, a feed material for step (a) above, may be derived, for example, by the chlorofluorination of hexachloropropylene. At least a portion of the $\text{CF}_3\text{CClFCF}_3$ is derived in accordance with step (d) above.

Figure 1 is illustrative of one method of practicing this invention.

15 Referring to Figure 1, a feed mixture comprising hexachloropropylene (i.e., $\text{CCl}_2=\text{CCl}_2$, or HCP), chlorine and hydrogen fluoride and where the HF:HCP molar ratio is about 3:1, or more (the Cl_2 :HCP ratio is typically about 1:1, or more), is passed through line (110) into reactor (100). Liquid phase, vapor phase or trickle bed reactors can be used. For the liquid phase and trickle bed reactors
20 the reaction temperature is at least about 25°C. The trickle bed reactors are usually packed, e.g., with carbon, or can contain bubble trays; both modes are well known in engineering practice. For the vapor phase reactors, which can be either empty or packed (e.g., with carbon), the minimum reaction temperature is at least 150°C. The $\text{CCl}_2=\text{CCl}_2\text{CF}_3$ starting material of step (a) can also be obtained by
25 the chlorofluorination reaction of 2-fluoropropane over a divalent cobalt on an activated carbon catalyst as described in U.S. Pat. No. 3,865,885.

The reactor effluent from chlorofluorination reactor (100) comprising 1,1,2-trichloro-3,3,3-trifluoropropene-1 (i.e., $\text{CCl}_2=\text{CClCF}_3$ or FC-1213xa), chlorine, HF and HCl is passed through line (120) into line (510) where it is
30 combined with the reaction effluent from reactor (500). The reactor (500) effluent comprises 2-chloro-1,1,1,2,3,3,3-heptafluoropropane (i.e., $\text{CF}_3\text{CClFCF}_3$ or CFC-217ba), HCl and HF.

The combined (100) and (500) reactor effluents are sent to reactor (200) which is maintained at a temperature within the range of about 250°C to about
35 325°C. Reactor (200) is packed with a catalyst comprising trivalent chromium. Additional HF may be added, if required. A preferred catalyst is Cr_2O_3 prepared by the pyrolysis of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ as described in U.S. Patent No. 5,036,036.

The reactor (200) effluent comprising HF, $\text{C}_3\text{Cl}_3\text{F}_3$, $\text{C}_3\text{Cl}_2\text{F}_6$ and C_3ClF_7 is sent through line (210) into distillation column (300). The $\text{C}_3\text{Cl}_3\text{F}_3$ component

WO 99/51553

PCT/US99/07230

is mainly composed of $\text{CClF}_2\text{CCl}_2\text{CF}_3$, $\text{CCl}_2\text{FCClF}_2$ and a small amount of $\text{CClF}_2\text{CF}_2\text{CClF}_2$. The $\text{C}_3\text{Cl}_2\text{F}_6$ component is mainly composed of $\text{CF}_3\text{CCl}_2\text{CF}_3$ and $\text{CClF}_2\text{CClF}_2$ and small amounts of $\text{CClF}_2\text{CF}_2\text{CClF}_2$. The C_3ClF_7 component is mainly composed of $\text{CF}_3\text{CClF}_2\text{CF}_3$. HCl and other low boiling components are removed through line (320) and the remainder of the reactor (200) effluent is sent through line (310) into a second distillation column (400). The bottom fraction from column (400) which comprises HF, $\text{C}_3\text{Cl}_3\text{F}_3$ and $\text{C}_3\text{Cl}_2\text{F}_6$ is sent through line (430) into reactor (500) which is maintained at a temperature of at least about 375°C . The reactor is packed with a catalyst comprising trivalent chromium. A preferred catalyst is the above-described Cr_2O_3 prepared by pyrolysis of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. The effluent from reactor (500) comprising HCl, HF and CFC-217ba is removed through line (510) and sent to reactor (200).

HF/CFC-217ba azeotrope is removed from the top of column (400) through line (410). HF/CFC-217ba azeotrope is passed through line (420) into catalytic reactor (600) along with hydrogen which is fed through line (610). The reactor (600) product is removed through line (620) and comprises, HCl, HFP, hexafluoropropylene (i.e., $\text{CF}_3\text{CF}=\text{CF}_2$ or HFP) and 1,1,1,2,3,3,3-heptafluoropropane ($\text{CF}_3\text{CHF}_2\text{CF}_3$ or HFC-227ea). The hydrogenolysis of step (c) may be conducted in the presence of HF. HFP and HFC-227ea can be isolated by conventional means. A portion of the azeotrope can be taken off through line (410) for other uses (e.g., the manufacture of $\text{CF}_3\text{CF}_2\text{CF}_3$).

The fluorination catalyst employed in steps (a) and (d) of the process of the invention may be supported or unsupported. Any of the fluorination catalysts described in the prior art may be used such as oxides, halides and oxyhalides of aluminum, cobalt, manganese, iron and particularly chromium. Suitable chromium-containing catalysts include oxide, hydroxide, oxyhalide, halides, inorganic acid salts, basic chromium fluorides and especially preferred are the chromium oxide catalysts described in U.S. Pat. No. 5,036,036. The catalysts may be given a prefluorination treatment by passing hydrogen fluoride, with or without an inert diluent such as nitrogen, over the catalyst at a temperature within the range of about 250 to 450°C prior to use.

The operating pressure of the process of the invention is dependent on the product isolation scheme employed and is generally within the range of from about 101 kPa to about 5000 kPa.

The reaction zone of steps (A) and (d) may consist of one or two reactors. CFC-217ba may be reacted with hydrogen to form a product comprising HFP and HFC-227ea by contacting the CFC-217ba with hydrogen at an elevated temperature in the vapor phase over a catalyst comprising at least one component selected from the group consisting of elemental metals, metal oxides, metal

WO 99/51553

PATENT/US99/07230

halides and metal oxyhalides; wherein the metal of said hydrodehalogenation catalyst component is selected from copper, nickel, chromium and mixtures thereof and the halogen of said halides and said oxyhalides is selected from fluorine, chlorine and mixtures thereof. Greater details of the reaction with hydrogen are described in U.S. Patent No. 5,057,634 which is incorporated herein by reference. Another useful catalyst comprises a three-dimensional matrix carbonaceous material such as that described in U.S. Patent No. 4,978,649.

Alternatively, CFC-217ba can be converted to a product comprising HFC-227ea and HFP by contacting CFC-217ba with hydrogen at an elevated temperature in the vapor phase over a catalyst comprising at least one metal selected from the group consisting of rhenium, ruthenium, rhodium and palladium. The reaction temperature for these metal-containing catalysts is at least about 100°C. The reaction temperature when other catalysts are used is normally at least about 300°C. In any case, the reaction temperature is normally less than 500°C.

The reaction pressure is normally within the range of about 100 kPa to about 7000 kPa. Typically, the mole ratio of hydrogen to CFC-217ba is from 0.5:1 to 25:1, preferably from 1:1 to 5:1.

Those skilled in the art will recognize that since the drawings are representational, it will be necessary to include further items of equipment in an actual commercial plant, such as pressure and temperature sensors, pressure relief and control valves, compressors, pumps, storage tanks and the like. The provision of such ancillary items of equipment would be in accordance with conventional chemical engineering practice.

The reaction zone and its associated feed lines, effluent lines and associated units should be constructed of materials resistant to hydrogen fluoride and hydrogen chloride. Typical materials of construction, well-known to the fluorination art, include stainless steels, in particular of the austenitic type, the well-known high nickel alloys, such as Monel® nickel-copper alloys, Hastelloy® nickel-based alloys and, Inconel® nickel-chromium alloys, and copper-clad steel.

Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed as merely illustrative, and do not constrain the remainder of the disclosure in any way whatsoever.

WO 99/31353

PCT/US99/07230

EXAMPLESLEGEND

	13 is CClF_3	23 is CHF_3
	112 is $\text{CCl}_2\text{FCCl}_2\text{F}$	113 is $\text{CCl}_2\text{FCClF}_2$
5	114 is $\text{CClF}_2\text{CClF}_2$	115 is CClF_2CF_3
	125 is CHF_2CF_3	214ab is $\text{CCl}_2\text{FCCl}_2\text{CF}_3$
	215aa is $\text{CClF}_2\text{CH}_2\text{CF}_3$	215bb is $\text{CCl}_2\text{FCClF}_2\text{CF}_3$
	215ca is $\text{CCl}_2\text{FCF}_2\text{CClF}_2$	216aa is $\text{CF}_3\text{CCl}_2\text{CF}_3$
	216ba is $\text{CClF}_2\text{CClF}_2\text{CF}_3$	216ca is $\text{CClF}_2\text{CF}_2\text{CClF}_2$
10	217ba is $\text{CF}_3\text{CClF}_2\text{CF}_3$	217ca is $\text{CClF}_2\text{CF}_2\text{CF}_3$
	218 is $\text{CF}_3\text{CF}_2\text{CF}_3$	226da is $\text{CF}_3\text{CHClCF}_3$
	226ea is $\text{CClF}_2\text{CHF}_2\text{CF}_3$	227ea is $\text{CF}_3\text{CHF}_2\text{CF}_3$
	236ea is $\text{CHF}_2\text{CHF}_2\text{CF}_3$	236fa is $\text{CF}_3\text{CH}_2\text{CF}_3$
	1213xa is $\text{CCl}_2=\text{CClCF}_3$	1214 is $\text{C}_3\text{Cl}_2\text{F}_4$
15	1215 is C_3ClF_5	1215xc is $\text{CF}_2=\text{CClCF}_3$
	1225zc is $\text{CF}_2=\text{CHCF}_3$	HFP is $\text{CF}_3\text{CF}=\text{CF}_2$
	CT is contact time	P is pressure
	T is temperature	

General Procedure for Product Analysis

- 20 The following general procedure is illustrative of the method used. Part of the total reactor effluent was sampled on-line for organic product analysis using a Hewlett Packard HP 5890 gas chromatograph equipped with a 20' (6.1 m) long x 1/8" (0.32 cm) diameter tubing containing Krytox[®] perfluorinated polyether on an inert carbon support and within a flame ionization detector. The helium flow was 25 35 mL/min. Gas chromatographic conditions were 70°C for an initial hold period of three minutes followed by temperature programming to 180°C at a rate of 6°C/minute.

- 30 The bulk of the reactor effluent containing organic products and also inorganic acids such as HCl and HF was treated with aqueous caustic prior to disposal.

EXAMPLE 1Chlorofluorination of FC-1213xa

- 35 Chromium oxide (47.25 g, 35 mL, 10-20 mesh, (2.0-0.84 mm)), obtained from the pyrolysis of ammonium dichromate prepared according to the procedure described in U.S. Pat. No. 5,036,036, was placed in a 5/8" (1.58 cm) diameter Inconel[®] nickel alloy reactor heated in a fluidized sand bath. It was heated to 175°C in a flow of nitrogen (50 cc/min) at which time HF flow (50 cc/min) was also started through the reactor. After 15 minutes, the nitrogen flow was decreased to 20 cc/min and the HF flow increased to 80 cc/min. The reactor

WO 99/31553

PCT/US99/07230

temperature was gradually increased to 400°C during a 2 hour period and maintained at 400°C for an additional 30 minutes. At the end of this period the reaction was brought to the desired operating temperature for catalyst evaluation under a nitrogen flow.

- 5 The results of the chlorofluorination reaction are shown in Table 1 in area %.

T °C	Molar Ratio HF:1213xa:Cl ₂	C.T. Sec.	TABLE I					% Others
			% 217ba	% 226da	% 216aa	% 216ba	% 215aa	
250	20:1:2	60	0.3	1.8	10.1	9.9	74.9	3.0
260	20:1:2	60	0.5	2.5	15.6	10.8	67.8	2.8
260	20:1:4	60	0.5	0.7	10.6	13.2	72.4	2.6
260	10:1:2	60	0.2	0.5	5.7	9.7	82.4	1.7
260	20:1:4	40	0.5	0.8	8.5	11.8	76.2	2.3
275	20:1:2	30	1.1	2.5	23.4	12.4	57.8	2.8
275	20:1:2	60	1.0	2.8	37.8	11.2	54.9	2.4
275	20:1:4	15	1.5	1.1	16.0	14.9	64.4	2.1
300	10:1:2	30	1.3	1.1	45.7	9.5	40.9	1.5
300	20:1:2	30	3.1	1.9	48.3	12.8	31.6	2.2
300	20:1:2	15	3.4	2.7	45.4	11.4	34.6	2.5
325	6:1:2	30	3.9	0.0	80.7	9.7	4.7	1.0

Others include mostly 1215, as well as 113, 114, 115, 1214, 215ca, 216ca and 217ca.

EXAMPLE 2

Chlorofluorination of FC-1213xa

The reactor used in Example 1 was charged with a 20% CrCl₃/carbon catalyst (6.15 g, 15 mL, 10-20 mesh, (2.0 0.84 mm)), prepared as described in Example 1 of U.S. Pat. No. 3,632,834, and activated as described above in Example 1.

The contact time for each run was 15 seconds. The results of the chlorofluorination reaction are shown in Table 2 in area %.

WO 99/51553

PCT/US99/07230

TABLE 2

T °C	Molar Ratio HF:1213xa:Cl ₂	% 216aa	% 216ba	% 1214	% 215aa	% 215bb	% 1213xa	% 214ab	% Others
300	20:1:4	4.0	0.2	6.5	19.5	6.9	61.3	0.0	1.9
325	20:1:4	3.7	0.5	3.7	39.1	7.1	39.7	0.0	1.3
325	20:1:2	14.6	0.4	3.7	36.1	6.6	37.2	0.0	1.4
350	20:1:4	16.1	1.0	3.1	50.7	7.9	0.0	19.1	1.9
350	6:1:1	13.6	0.3	2.5	51.9	4.3	1.2	25.0	1.2

Others include mostly 1215, as well as 13, 112, 113, 216ca, 226da and

217ha.

EXAMPLE 3Fluorination of FC-216aa

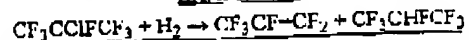
- 5 The reactor and catalyst treatment were the same as those described in Example 1. A fresh sample of chromium oxide catalyst was used.

The contact time for each run was 30 seconds. The results of the fluorination reaction are shown in Table 3 in mol %.

TABLE 3

T °C	Molar Ratio HF:216aa	% 218	% 217ba	% 1215	% 226da	% 216aa	% Others
375	4:1	0.2	7.4	0.6	0.7	90.2	0.8
400	4:1	0.6	18.2	0.7	0.9	78.7	0.9
400	8:1	0.6	22.2	1.0	0.9	74.5	0.8
400	12:1	0.6	23.8	1.3	0.9	72.4	0.9
400	20:1	0.6	28.2	1.8	1.7	66.5	1.2
425	20:1	1.3	53.7	1.6	1.7	39.7	1.9

- 10 Others include mostly 23, 115, 125, 1214, 1215, 227ca, 216ba and 217ca.

EXAMPLE 4

A 15" (38.1 cm) X 3/8" (0.95 cm) O.D. Inconel™ 600 nickel alloy U-tube reactor was charged with 8% Res/Acid-Washed Carbon (2.4 g, 6.25 mL). The

- 15 H₂:CFC-217ba molar ratio was 2:1. Results (in mol %) at various conditions are shown in Table 4.

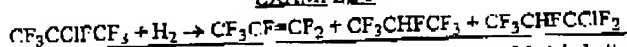
WO 99/51553

PCT/US99/07230

TABLE 4

T °C	P psig (kPa)	CT min.	% Conv. 217ba	% Sel. HFP	% Sel. 1225ec	% Sel. 217ea	% Sel. 226ca	% Sel. Other
260	0 (101)	1.1	100	23	0.6	71	3.7	1.3
260	38 (363)	1.3	98	18	0.6	73	6.6	1.3
260	100 (791)	1.1	80	16	0.5	76	6.2	1.3
280	0 (101)	1.0	100	25	1.7	68	2.6	2.3
280	30 (308)	1.0	100	18	1.8	71	6.4	3.0
280	100 (791)	2.1	100	7	2.8	69	16.4	4.5
300	0 (101)	0.3	100	25	1.6	69	2.0	2.2
300	0 (101)	0.5	100	26	2.4	67	1.7	2.9
300	0 (101)	1.0	100	23	4.0	66	1.7	4.4

EXAMPLE 5



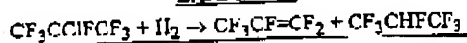
A 15" (38.1 cm) X 1/4" (0.64 cm) O.D. Hastelloy™ C-276 nickel alloy

- 5 11-tube reactor was charged with 1% Ru/Acid-Washed Carbon calcined at 925°C (2.59 g, 6.25 mL). The reaction pressure was 0 psig (101.3 kPa). Results (in mol %) at various conditions are shown in Table 5.

TABLE 5

T °C	Mol H ₂ /217ba	CT sec.	% Conv. 217ba	% Sel. HFP	% Sel. 227ea	% Sel. 236fa	% Sel. 226ca	% Sel. Other
325	2	31	100	4	43	1.5	43.4	8.0
325	2	16	80	13	36	0.6	42.0	3.6
350	2	15	85	18	36	1.2	40.1	3.5
325	4	30	76	29	40	0.9	27.2	3.3
325	4	6	23	58	35	0.2	4.1	3.1
350	4	6	24	59	32	0.7	3.0	4.5
350	4	3	6	67	24	0.9	0.4	7.7
360	4	3	5	64	25	1.1	0.2	9.9

EXAMPLE 6



A 15" (38.1 cm) X 3/8" (0.95 cm) O.D. Inconel™ 600 nickel alloy U-tube reactor was charged with 1% Ru/Acid-Washed Carbon (1.9 g, 5.25 mL). The reaction pressure was 0 psig (101.3 kPa). Results (in mol %) at various conditions

- 15 are shown in Table 6.

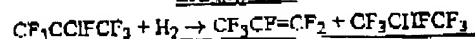
WO 99/51553

PCT/US99/07230

TABLE 6

T °C	Mol H ₂ :217ba	CT min.	% Conv. 217ba	% Sel. HFP	% Sel. 227ea	% Sel. 226ea	% Sel. Other
200	4	0.30	84	7	74	5	13
175	4	0.32	46	10	72	4	15
213	2	0.30	81	9	75	6	9
200	1	0.31	50	15	74	5	6

EXAMPLE 7



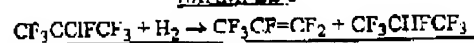
- 5 A 15" (38.1 cm) X 1/4" (0.64 cm) O.D. Inconel™ 600 nickel alloy U-tube reactor was charged with carbon which was a three-dimensional matrix carbonaceous material (2.36 g, 6.25 mL, 20-30 mesh (0.84-0.59 mm)). The reaction pressure was 0 psig (101.3 kPa) for the first Table 7 entry and 30 psig (308 kPa) for all the others. The H₂:CFC-217ba molar ratio was 4:1 for the first entry and 16:1 for all the others. Results (in mol %) at various conditions are
- 10 shown in Table 7.

TABLE 7

T °C	CT min.	% Conv. 217ba	% Sel. HFP	% Sel. 227ea	% Sel. 226ea	% Sel. 1215xc
350	0.10	10	65	27	4	0.9
350	0.12	11	61	28	8	0.8
370	0.12	12	61	27	9	1.0
400	0.12	15	59	27	10	1.2
400	0.06	12	68	24	5	0.7
425	0.06	14	68	24	5	0.8
475	0.05	24	63	27	7	0.7
450	0.05	13	62	31	5	0.4
450	0.11	13	52	40	6	0.4

Arbent.

EXAMPLE 8



- 15 The same reactor and catalyst as used for Example 7 was used. The reaction pressure was 0 psig (101.3 kPa) and the H₂:CFC-217ba molar ratio was 4:1. Results (in mol %) at various conditions are shown in Table 8.

WO 99/51553

PCT/US99/07230

TABLE 8

T °C	CT min.	% Conv. 217bs	% Sel. HFP	% Sel. 227ea	% Sel. 236ca	% Sel. 1215xc	% Sel. Others
325	0.10	14	43	20	2	0.7	1.6
350	0.10	11	62	28	4	1.2	2.6
350	0.05	9	65	27	5	0.9	3.0
350	0.50	9	56	32	6	2.4	4.4

Carbon.

WO 99/81863

PCT/US99/07230

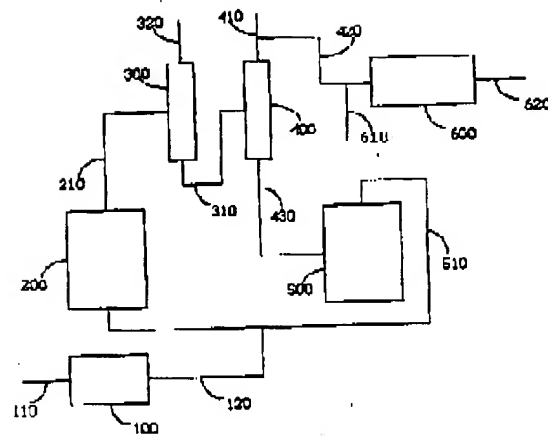
CLAIMS

1. A process for the manufacture of $\text{CF}_2=\text{CFCF}_3$ and $\text{CF}_3\text{CHFCHF}_3$, comprising:
- 5 (a) feeding $\text{CCl}_2=\text{CClCF}_3$, HF and Cl_2 to a first reaction zone containing a catalyst comprising trivalent chromium and operating at a temperature of at least 250°C , but not more than about 325°C , to produce a reactor effluent comprising $\text{C}_3\text{Cl}_3\text{F}_5$, $\text{C}_3\text{Cl}_2\text{F}_6$, $\text{CF}_3\text{CClFCHF}_3$, HCl and HF;
- 10 (b) distilling the reactor effluent of (a) to produce (i) a low boiling stream comprising HCl, (ii) a reactant stream comprising an azeotrope of $\text{CF}_3\text{CClFCHF}_3$ and HF and (iii) a high-boiling stream comprising $\text{C}_3\text{Cl}_2\text{F}_6$ and $\text{C}_3\text{Cl}_3\text{F}_5$;
- 15 (c) reacting the $\text{CF}_3\text{CClFCHF}_3$ of reactant stream (ii) with hydrogen in the presence of a catalyst to produce a mixture comprising $\text{CF}_2=\text{CFCF}_3$ and $\text{CF}_3\text{CHFCHF}_3$;
- 20 (d) feeding the $\text{C}_3\text{Cl}_2\text{F}_6$ and $\text{C}_3\text{Cl}_3\text{F}_5$ of high boiling stream (iii) along with HF to a second reaction zone containing a catalyst comprising trivalent chromium and operating at a temperature of at least about 375°C to produce a reaction product comprising $\text{CF}_3\text{CClFCHF}_3$ and HF; and
- (e) recycling the reaction product of (d) to the first reaction zone.
2. The process of Claim 1 wherein the $\text{CCl}_2=\text{CClCF}_3$ of (a) is derived by the chlorofluorination of $\text{CCl}_2=\text{CClCCl}_3$.
3. The process of Claim 1 wherein the hydrogenolysis of (c) is conducted in the presence of HF.

WO 99/51553

PCT/US99/07230

FIG 1



INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/US 99/07230

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 6 C07C17/087 C07C17/21 C07C17/23		
According to International Patent Classification (IPC) or to local national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC 6 C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Relation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 043 491 A (WEBSTER JAMES L ET AL) 27 August 1991 cited in the application see the whole document	1-3
Y	EP 0 530 989 A (HOECHST AG) 5 May 1993 see the whole document	1-3
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "C" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document relating to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "X" later document published after the international filing date or priority date and not in conflict with the application but cited to underpinning the principle or theory underlying the invention "Y" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Z" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
2 July 1999		12/07/1999
Name and mailing address of the ISA European Patent Office, P.O. 5018 Patankian 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2940, Tx. 21 551 see nt, Fax (+31-70) 340-3015		Authorized officer Janus, S

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Int'l Application No.

PCT/US 99/07230

Patent document cited in search report	Publication date	Patent family members	Publication date
US 5043491 A	27-08-1991	CA 2032250 A	20-06-1991
		DE 69010171 D	28-07-1994
		DE 69010171 T	05-01-1995
		CP 0434407 A	26-06-1991
		JP 2613685 B	28-05-1997
		JP 4117335 A	17-04-1992
EP 0539989 A	05-05-1993	CA 2081813 A	02-05-1993
		DE 59208629 U	24-07-1997
		ES 2104790 T	16-10-1997
		JP 5221894 A	31-08-1993
		SG 44743 A	19-12-1997

Form PCT/ISA/Z11 (patent family members) (July 1990)